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COATING and CHEMICAL LABORATORY

CCL REPORT NO. 136

EXPLORATION OF NEW METHODS FOR PREVENTING GALVANIC CORROSION BETWEEN MAGNESIUM AND STEEL

BY

LT. DONALD K. STELLING

AMCMS CODE NO. 5026.11.84205
DA PROJECT 593-32-007

8 JANUARY 1963

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MARYLAND

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AUTHOR: Donald K. Stelling
DONALD K. STELLING, Chemist
2nd Lt. Ord. Corps
Paint, Varnish & Lacquer Branch

REVIEWED BY: Melvin H. Sandler
MELVIN H. SANDLER
Chief, Paint, Varnish
& Lacquer Branch

APPROVED BY: C F Pickett
C. F. PICKETT, Technical Director
Coating and Chemical Laboratory

ABSTRACT

An investigation was conducted to explore new methods of treating magnesium-steel couples after the two metals had been assembled and placed in electrical contact with each other. A phosphate anodizing treatment, prepared with this objective in mind, proved to be ineffective when applied to such couples. The treatment seemed to offer considerable corrosion resistance to magnesium alone when the operating conditions of the treatment were controlled within close limits.

I. INTRODUCTION

The accelerated corrosion rate observed with magnesium when coupled to a dissimilar metal is a problem of great concern to the defense industry. With missile systems and lightweight airborne equipment becoming increasingly more complex, design requirements oftentimes call for an assembly of dissimilar metals, such as magnesium and steel. Electrical contact between the two metals is oftentimes established and because of the difference in the relative positions of the two metals in the EMF series, a galvanic cell is created. When the assembly is exposed to moisture and electrolyte, as in a saline atmosphere, galvanic corrosion results. The most effective method of preventing galvanic corrosion is to insulate the faying surfaces of the two metals to prevent the formation of the galvanic cell. However, when press fits between dissimilar metals are required, this is not possible. There is a need for an effective treatment that can be applied to dissimilar metal couples (particularly magnesium and steel) after assembly that will prevent or appreciably retard the affects of galvanic corrosion. A recently developed stannate treatment offers a step in this direction. The treatment involves immersing a magnesium-steel assembly for a minimum of twenty minutes in a bath containing potassium stannate (K_2SnO_3), sodium hydroxide ($NaOH$), sodium acetate ($NaC_2H_3O_2$), and tetrasodium pyrophosphate ($Na_4P_2O_7$) maintained between 180°F and 212°F. Although the treatment affords some protection against galvanic corrosion, it has not provided the desired degree of protection.

A hypothesis exists stating the rate of corrosion of a metal depends, in most cases, on the permeability of the surface film to the reactants. The porosity of the film appears to depend on the relative volume of the film compared to the volume of the metal from which it is formed, i.e, Wd/awD where:

- W = molecular weight of the metallic compound forming the film (of formula MaXb)
- D = density of the compound forming the film
- W = atomic weight of metal
- d = density of the metal
- M = metal anion of the compound forming the film
- X = cation of the compound forming the film
- a = number of anions per molecule of film compound
- b = number of cations per molecule of film compound

If this ratio is greater than one, the film tends to be protective; if the ratio is less than one, the film is porous and non-protective. The ratio for magnesium oxide (MgO), formed on a magnesium surface when exposed to moisture, is 0.64 and thereby accounts for the non-protective character of the film formed by corrosion product. On the other hand, magnesium treated with chromic acid forms a corrosion resistant film composed of magnesium chromate ($MgCrO_4 \cdot 7H_2O$) for which the ratio is 11.3. Similarly, the film of magnesium fluoride (MgF_2) formed when magnesium is treated by hydrofluoric acid produces a ratio of 1.49 indicating the film to be protective, which indeed it is.

If this hypothesis is valid for all films, then a magnesium surface film of magnesium phosphate ($Mg_3(PO_4)_2$), resulting from treatment with a $PO_4^{\equiv}$ solution, or a magnesium surface film of magnesium pyrophosphate ($Mg_2P_2O_7$), resulting from treatment with $P_2O_7^{=}$ solution, should be protective since their

ratios are 4.0 and 3.9 respectively. Therefore, it was decided to conduct a number of laboratory tests whereby magnesium panels would be treated by phosphate and pyrophosphate solutions under various operating conditions including the application of an external EMF. If, a treatment could be developed that would successfully protect magnesium alone, it would then be tested on magnesium-steel couples since the phosphate and pyrophosphate treatments should also produce protective films on steel because the ratios for ferrous phosphate ($Fe_3(PO_4)_2$) and ($Fe_4(P_2O_7)_3$) are 8.9 and 12.0 respectively.

II. DETAILS OF TEST

These studies were conducted testing the applicability of various phosphating procedures on magnesium. After treatment, the panels were coated with 0.001 inch dry film of Military Specification MIL-P-15930 (Primer, Vinyl Zinc Chromate Type, Formula No. 120) air dried 72 hours, scored, and then exposed to 20% salt spray (operated according to Federal Test Method Standard No. 141, method 6061). The test panels were examined every 24 hours and evaluated for corrosion resistance.

Initially, three series of AZ31B magnesium alloy panels were given a light zinc phosphating treatment according to Military Specification TT-C-490, type I. For each series of panels, the application procedure was varied slightly (see Table I).

Another test (Table II) was conducted whereby two series of AZ31B alloy panels were spray treated by phosphating solutions conforming to Military Specification TT-C-490, type II.

A number of cursory laboratory tests were also performed whereby magnesium panels were treated by solutions of NaH_2PO_4 under various operating conditions including the application of an external EMF. Tests involving baths containing $Na_2P_2O_7$ and mixtures of $Na_2P_2O_7$ with NaH_2PO_4 were also conducted. The results of this effort showed that an anodizing bath containing $NaH_2PO_4 \cdot H_2O$ at a concentration of 13.7 gms/liter offered the most promising results. The phosphate anodizing process consisted of connecting the magnesium component to the anode of a D. C. source and using one or two steel plates immersed in the bath as the cathode. A current density of 16 amps/sq.ft. was applied for a period of ten minutes during which time the potential remained rather steady around 20 volts, dropping possibly a maximum of two volts. The bath was maintained at room temperature and the pH rose during the operation from about 5.0 to 5.5 where it reached a plateau. Studies were made to determine the operating limits by varying the bath concentration between 0.5 to 1.0 moles NaH_2PO_4/liter of water, the pH from 4.3 to 6.9, the current desnity from 8 amps/sq.ft. to 60 amps/sq.ft. and operating times from 8 to 25 minutes (see Table III).

This phosphate anodizing treatment was compared with three other proprietary magnesium treatments used quite extensively in industry, namely a chemical pretreatment conforming to Specification MIL-M-3171, Type III; an anodic pretreatment conforming to Specification MIL-M-45202 (Ord), type I, class C; and a chemical treatment consisting of a five minute immersion at room temperature in a bath containing chromic acid (CrO_3) and calcium sulfate ($CaSO_4$) (see Table IV).

The phosphate anodizing treatment was also evaluated on magnesium-steel couples. Test specimens were prepared by placing a steel bolt through a magnesium panel and treating the specimen after assembly (see Table V).

III. DISCUSSION

The TT-C-490, type I zinc phosphate immersion produced a loose, powdery coating bluish-gray in appearance. Upon removal of the powder, a dark, adherent coating was noticed on the immediate surface. The spray zinc phosphate treatment produced a coating that was free from the powdery deposit and similar in appearance to the dark undercoating of the immersion treated panels. The salt spray results shown in Table I indicate that the immersion treatment offers only slight corrosion resistance whereas the spray method offers none.

The TT-C-490, type II treatment produced only slight discoloration on the panel surfaces. The results in Table II show that the four minute spray method afforded considerably more protection than the two minute spray.

The phosphate anodizing treatment produces a surface film which is dark & grainy in appearance. Unfortunately, the bath becomes readily depleted and in doing so, a white, powdery precipitate forms on the edges of the test panels giving the appearance of corrosion product. This precipitate is easily washed off upon subsequent rinsing and seems to have no detrimental effects upon the performance of the coating, nevertheless, it produces a rough, uneven surface. This same observation was made when the bath was operated at a high pH around 6.8, even though excellent corrosion resistance was noted (see Table III). This effect became worse upon subsequent treatments in the same bath. In fact, it was found that operating conditions varying slightly from a pH of 4.3 to 5.5, a current density of 16 amps/sq.ft., and an operating time of 10 to 15 minutes made the treatment considerably less effective.

When strict control over the operating variables is exercised, however, this phosphate anodizing treatment seems to offer considerable protection to magnesium alone. As can be seen in Table IV, when compared with three proprietary treatments, it offered the best corrosion resistance, being somewhat better than MIL-M-45202 and considerably better than MIL-M-3171 and the chromic acid/calcium sulfate immersion treatment.

Unfortunately, the phosphate anodizing treatment is not applicable to magnesium-steel couples. The results in Table V demonstrate the ineffectiveness of the treatment for such applications.

IV. SUMMARY

Although the phosphate anodizing treatment has been demonstrated to be non-applicable to magnesium-steel couples, further testing and development should be conducted before it can be accepted as an effective procedure for magnesium alone. Such efforts should be concentrated in(a) determining more closely the operating limits of the bath,(b) evaluating more extensively the effectiveness of the treatment by comparing it with many proprietary treatments, (c) eliminating the deposit of white precipitate on the edges of the test panels and increasing the life of the phosphate bath.

Of course the greatest efforts in future studies should be directed to develop a method of preventing galvanic corrosion. The ideal treatment would be one that contains a self-healing ingredient which, when the film is scored, would leach out of the coating and treat the newly exposed metal. Without this particular feature, it would be thermodynamically impossible for a scored bimetallic assembly to resist corrosion.

Because of the difficulty encountered in attempting to develop an aqueous treatment for magnesium-steel couples, a study should be initiated into the use of organic media for treating bimetallic assemblies. Such a study would involve much basic research since limited information can be found in this field.

V. REFERENCES

1. Military Specification MIL-P-15930 Primer, Vinyl-Zinc Chromate Type (Formula 120).

2. Federal Test Method Standard No. 141 - Paint, Varnish, Lacquer and Related Materials, Methods of Inspection, Sampling and Testing.

3. Military Specification TT-C-490 Cleaning Methods and Pretreatment of Ferrous Surfaces for Organic Coatings.

4. MIL-M-3171 Magnesium Alloy, Processes for Corrosion Protection of.

5. MIL-M-45202 (Ord) Magnesium Alloys, Anodic Treatment of.

APPENDIX

TABLE I

SALT SPRAY RESULTS (HOURS TO FAILURE)

PHOSPHATE PRETREATMENT[1] TT-C-490, TYPE I ON MAGNESIUM

No Pretreatment	One minute @ 180°F Immersion process	Five minutes @ 180°F Immersion process	One minute @ 150°F Spray process
24	72[2]	96[2]	24
24	72[2]	72[2]	24
	96[2]	72[2]	
	72[2]	72[2]	
	24	24	

[1]After pretreatment test panels were coated with one mil dry film of primer conforming to Specification MIL-P-15930, Primer, Vinyl Zinc Chromate Type, Formula No. 120.

[2]The loose powdery crystals formed on the surface by the immersion process were removed prior to application of primer.

TABLE II

SALT SPRAY RESULTS (HOURS TO FAILURE)

PHOSPHATE PRETREATMENT[1] TT-C-490, TYPE II ON MAGNESIUM

No Pretreatment	Two minutes @ 150°F Spray process	Four minutes @ 150°F Spray process
24	96	120
24	72	144
	96	216
	96	216
		144

[1]After pretreatment test panels were coated with one mil dry film of primer conforming to Specification MIL-P-15930 Primer, Vinyl Zinc Chromate Type, Formula No. 120.

TABLE III

SALT SPRAY RESULTS

PHOSPHATE ANODIZING[1] ON MAGNESIUM

NaH_2PO_4 Concentration (moles/liter)	pH	Current density (amps/sq.ft.)	Operating time (minutes)	Temperature °F	Hours Exposure Before Failure
0.1	5.0	8.0	15	74	600
0.1	4.3	16.0	10	73	912
0.1	6.6	16.0	15	72	1008
0.1	6.9	24.0	10	74	912
0.5	4.0	16.0	15	73	792
0.5	4.4	60.0	8	75	600
0.1	4.3	16.0	10	75	792
0.1	5.0	12.0	25	77	600
0.1	5.0	12.0	20	78	600
0.1	5.4	12.0	20	80	552
0.1	5.5	16.0	10	82	912
0.1	5.5	16.0	10	82	792

[1]After pretreatment test panels were coated with one mil dry film of primer conforming to Specification MIL-P-15930 Primer, Vinyl Zinc Chromate Type, Formula No. 120.

TABLE IV

SALT SPRAY RESULTS (HOURS TO FAILURE)

PHOSPHATE ANODIZE VS PROPRIETARY PRETREATMENTS ON MAGNESIUM[1]

No Pretreatment	Phosphate anodize[2]	MIL-M-3171 Type III	MIL-M-45202(Ord) Type I, Class C	CrO_3+$CaSO_4$ Bath[3]
72	648	168	360	168
72	744	216	672	216
72	720	168	672	168
72	648	240	408	240
72	648	240	408	240
72	648	216	672	216

[1]After pretreatment test panels were coated with one mil dry film of primer conforming to Specification MIL-P-15930 Primer, Vinyl Zinc Chromate Type, Formula No. 120.

[2]Operating conditions: 0.1 mole/liter; pH = 5.0 to 5.5; current density 16 amps/sq/ft/; operating time 10 min. at room temperature.

[3]Five minute immersion in the bath at room temperature.

TABLE V

SALT SPRAY RESULTS (HOURS TO FAILURE)

PHOSPHATE ANODIZE ON MAGNESIUM-STEEL COUPLE[1]

No Pretreatment	Phosphate Anodize[2]
24	24
24	24
24	24
24	24
24	24
24	24

[1] Specimens were assembled prior to treating. After pretreatment they were coated with one mil dry film of primer conforming to Specification MIL-P-15930 Primer, Vinyl Zinc Chromate Type, Formula 120.

[2] Operating conditions: 0.1 mole/liter; pH 5.0 to 5.5, current density 16 amps/sq.ft. Operating time - 10 minutes at room temperature.

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